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Noxious Trace Gases in the Air Part I. Photochemical Smog

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16. ABSTRACT An outline of the photochemical smog problem is presented, with emphasis on the chemical reactions taking place in the polluted air. The chemistry is discussed in terms of (1) the organic pollutants, such as hydrocarbons, (2) the nitrogen containing pollutants, such as nitrogen dioxide, and (3) the interaction of these two families of pollutants with the production of noxious by-products, such as ozone and particulate matter.					
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Part I. Photochemical Smog

Noxious Trace Gases In The Air

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This article examines photochemical smog—a tropospheric phenomenon. A second article next month will discuss halogenated pollutants reacting with ozone—a stratospheric phenomenon. The two parts of the problem involve man-induced disturbances of the atmospheric ozone, but disturbances in opposite directions. Although ozone is created by pollution in the troposphere, ozone is destroyed by pollution in the stratosphere.

In Los Angeles after the second World War it became evident that something had gone wrong with the air. Deterioration had been going on since before the war, but by the early 1950s the increased amount of haze in the air was obvious to nearly everyone. It had become a rare day when the Santa Monica and San Gabriel Mountains could be seen clearly, and the air seemed to smell different than it had in earlier years. There was even a new sensation of eye irritation.

Farmers in the Los Angeles basin already knew that the city air was attacking their vegetables, flowers, and fruits. As a result, much of the early study of "smog" was carried out by plant pathologists. Biochemist A. J. Haagen-Smit of the California Institute of Technology was one of the first to understand that Los



Angeles smog differed from London fogs and most other cases of urban pollution. In Los Angeles, there were no large sources of smoke and fumes such as steel mills, coal-fired power plants, dumps, or coke ovens. Instead, it appeared that new substances were being formed in the air itself.

Haagen-Smit's early studies concentrated on the formation of ozone in the air. Ozone was detected by the simple but highly sensitive method of rubber cracking. A stretched rubber band would be exposed to the air for a specified time, and cracking resulting from oxidation would be measured under a microscope. These experiments not only cracked the rubber bands, they also "cracked" the mysterious case of the Los Angeles smog.

It became obvious early in the study of smog that the automobile and gasoline were likely major contributors to the pollution. It was shown in Haagen-Smit's laboratory that auto exhaust in the air produced ozone when irradiated with ultraviolet light. Studies in smog chambers at the laboratories of the Los Angeles Air Pollution Control District, the Stanford Research Institute, and the University of California, Riverside showed that auto exhaust in air exposed to sunlight could produce plant damage, eye irritation, and light scattering associated with smog. Many clues to the kinds of



On a smoggy day, the buildings of Manhattan (opposite) almost disappear in layers of smog and haze. In Los Angeles (left), helium-filled tetrons—air-borne bouys—are used to mark off sections of air for tracing and taking samples of smog

chemical reactions in the polluted Los Angeles air were also obtained at the Franklin Institute Laboratories in Philadelphia by researchers working with the technique of long-path infrared absorption spectroscopy. Although the case against auto exhaust as the basic cause of smog was well established by 1957, 20 years later details of the chemistry are still being worked out.

Atmospheric Chemistry

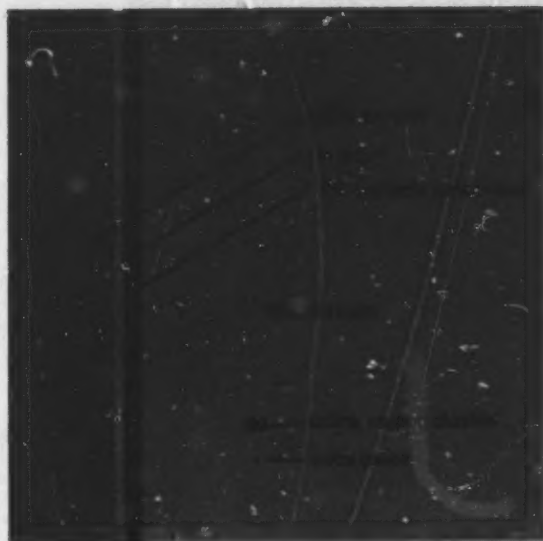
The smog problem gave great impetus to the study of atmospheric chemistry, but it was by no means its beginning. Atmospheric scientists were concerned with ozone and nitrogen oxides in the atmosphere long before the smog arose. The focus of atmospheric chemistry seems to have cycled up and down. Laboratory studies first were concerned with the general composition of the atmosphere, but concern then shifted to understanding processes in the stratosphere. The smog problem brought the emphasis back to the lower troposphere, and recently the problems of nuclear explosions, supersonic transport, and chlorofluorocarbon pollutants have once again focused concern on the stratosphere.

Air chemistry can be broadly divided into tropospheric chemistry and stratospheric chemistry. The troposphere is well-mixed and

quite homogeneous in the distribution of its trace gases. The stratosphere, on the other hand, is poorly mixed and nonuniform in its trace gases (Figure 1). The real atmosphere is of course more complex than the figure implies, with many interrelated physical and chemical processes. Distribution of trace gases, for example, is influenced by the pattern of turbulence which is the result of temperature gradients. Temperatures in turn depend on radiation absorption and emission, while the radiation exchange is controlled by the trace gases.

Temperature reversal marks the tropopause, where the troposphere becomes stratosphere. In the troposphere the decrease of temperature with increasing altitude causes an instability—colder, heavier air does not remain aloft, but tends to fall, causing turbulence. Above the tropopause, higher air is warmer and lighter than lower air, and there is much less mixing. Air movements in the stratosphere are much slower than those in the troposphere, but occur on a larger scale. Because photochemical formation and destruction of trace gases take place at the top of the stratosphere, the large, slow air movements lead to an unevenness in the concentrations of the stratospheric trace gases that appears within a larger pattern of layering. The layering of ozone (the ozonosphere) is shown by the density of dots in Figure 1.

Composition of the Lower Atmosphere



The diagram on the left shows major constituents of the atmosphere in terms of areas on the figure. The large blue area, 78%, gives the proportion of nitrogen (by volume). The area at the left, 19.5%, gives the proportion of oxygen. The narrower of the two strips (1%) is argon, and the other strip (1.5%-variable) is water vapor. The black square represents the 0.03% which is carbon dioxide. Finally, the area of the tiny speck is proportional to the sum of all other constituents—the trace gases. Many of these trace gases are variable, like the water, but they never add up to more than a few ppm of the total.

The diagram on the right shows in bar graph form the proportions of atmospheric trace gases—the composition of the "speck." The natural background amounts are shown in green, while the amounts resulting from man's influence are shown in purple. The figure illustrates an urban atmosphere polluted mainly by auto exhaust.

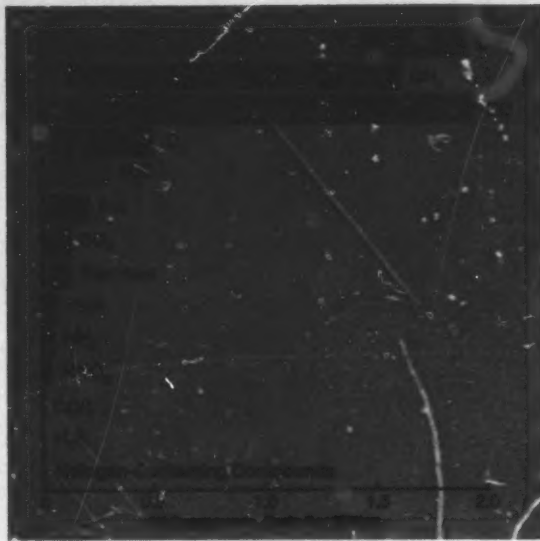
Methane, CH_4 , the simplest species of hydrocarbon, is the major organic compound in the air, about 1.4 ppm. Excess methane will be found in marshes, mines, and wherever there are natural gas leaks. The diagram shows a 25% excess, not unusual in cities.

CH_x is the organic matter that with the help of nitrogen oxides produces smog. In urban air, CH_x consists mainly of hydrocarbons from gasoline vapors and auto exhaust. The amount of CH_x in natural clean air is relatively small—less than 0.1 ppm.

The carbon monoxide bar shows a typical urban total of about 2 ppm, with about 95% being pollutant from auto exhaust. Like methane, CO takes part in the natural slow chemistry of the air, but it plays only a minor role in the photochemistry of smog.

Ozone, a vital natural component of the air, can increase 10-fold or more as a result of photochemistry in urban air, reaching the dangerous level of 0.5 ppm. Ozone is the principal noxious by-product of the urban photochemistry.

Nitrous oxide, N_2O , occurs naturally in the air at about 0.3 ppm and is produced by the action of bacteria on nitrogen-containing organic matter. N_2O is an inert species and does not take part in urban atmospheric photochemistry.



Within the total NO_x , nitric oxide, NO, and nitrogen dioxide, NO_2 , shift proportions during the day. The NO is produced in combustion and is released into the air in such effluents as auto exhaust and power plant fumes. Clean air contains NO_x at a few ppb. In the cities the NO_x concentration can reach several hundred ppb, leading to urban smog.

In amount, sulfur dioxide is a minor pollutant, but its effects are major. In urban areas the SO_2 comes from the sulfur in coal, oil, and gasoline. The natural SO_2 content of the air is very small—probably less than 1 ppb. In urban areas, SO_2 may reach 100 ppb or more. The undesirable effects of sulfur dioxide occur mainly after the compound is converted to fine particles of sulfate.

With regard to fine particles, the figure shows the total particulate mass in urban air to be quite small compared to the mass of gaseous pollutants. As in the case of the SO_2 gas, however, the effects are disproportionate with the mass.

PAN, peroxy acyl nitrates, is a family of oxidants produced in the atmosphere from the other pollutants. PANs are responsible for a good share of the undesirable effects of the smog such as plant damage and eye irritation.

Ammonia, produced in biological processes, is ubiquitous in the atmosphere. Its concentration usually runs to a few ppb, but this varies greatly. In urban areas the ammonia is likely to be rather fully used up in the formation of particles of ammonium sulfate and ammonium nitrate.

Nitric acid is formed in the lower atmosphere by the interaction of ozone, nitrogen dioxide, and water. The acid reacts with the ammonia gas and it also is readily taken up on surfaces. The concentration of gaseous nitric acid rarely reaches more than a few ppb.

Carbonyl sulfide, COS, occurs at about 0.5 ppb, and may be the major carrier of sulfur into the stratosphere. The reduced sulfur compounds like H_2S are produced in substantial amounts but also are quickly oxidized to SO_2 . The concentration in clean tropospheric air is much less than 1 ppb.

The last bar represents the total amount of all halogen-containing pollutants seen in the clean troposphere. This total falls between 1 and 2 ppb, a trivial amount. The effects of the halogenated pollutants, however, are of great concern.

Families of Trace Gases

Although the trace gases of the atmosphere have major significance, both optically and chemically, the actual amounts of these gases are extremely small (see page 10). Atmospheric chemists consider trace gases as members of the following principal family groups.

CH_x—Hydrocarbons and some other organics

NO_x—Nitrogen-containing compounds

SO_x—Sulfur-containing compounds

CO_x—Oxides of carbon

ClO_x—Chlorine-containing compounds

O_x—Forms of oxygen

These are approximate groupings, however, with some compounds falling in between. Carbonyl sulfide (COS), for example, is a hybrid of CO_x and SO_x. All families except ClO_x are involved in the formation of photochemical smog. All families except SO_x are involved in the control of stratospheric ozone.

The main photochemical action in the urban atmosphere involves the CH_x family and the NO_x family. These pollutants do not interact in the dark, but they interact markedly in the sunlit atmosphere. Most pollutants are in reduced form when they are emitted, and their transformations in the air then carry them up the scale of oxidation until they are finally removed in their highest oxidation state. Smog production runs on auto exhaust as the fuel, air as the oxidizer, and sunlight as the igniter.

Organic Compounds (CH_x)

Methane (CH₄), the predominant organic compound in the clean air, participates in the slow natural photochemistry of the air. But methane resists oxidation in the atmosphere better than other organic compounds with the exception of a few heavily halogenated man-made gases. Although methane does participate in the formation of natural background ozone, it plays no significant role in the formation of the excess ozone found in urban areas.

The nonmethane hydrocarbons in urban areas consist mainly of gasoline vapors and auto exhaust. Gasoline is a mixture of paraffinic hydrocarbons such as butanes, pentanes, and hexanes and aromatic hydrocarbons such as toluene and the xylenes. While auto exhaust includes some gasoline compounds in their original form, more importantly it includes compounds that have been partially dehydrogenated (olefins) such as ethylene, propylene, and isobutylene. These molecules are highly reactive in the atmosphere, contributing to the smog in much higher degree than most other organic compounds.

Hydrocarbons participate in smog formation by a complex interaction with the nitrogen ox-

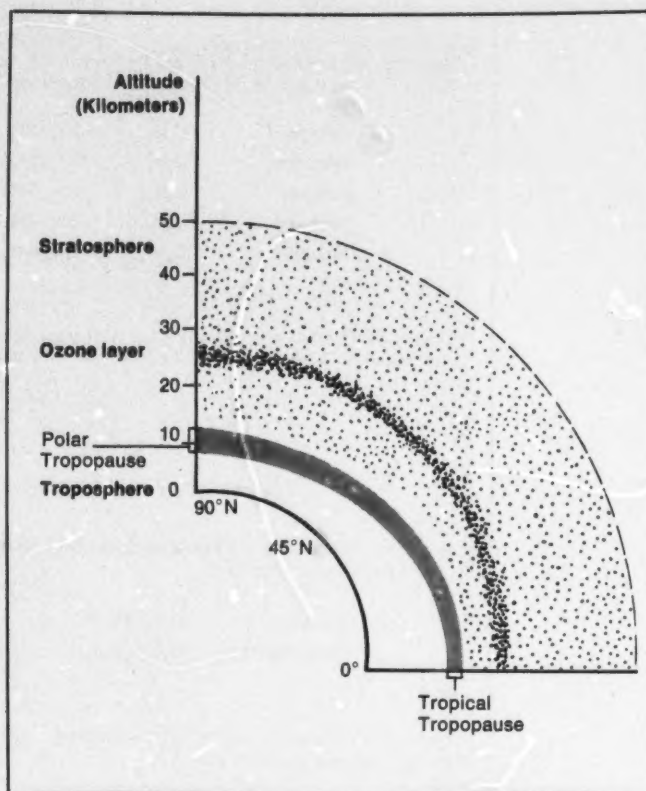
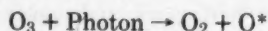


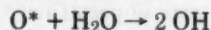
Figure 1. The atmosphere is broadly divided into troposphere and stratosphere. Within the troposphere, temperature decreases with increasing altitude, but in the stratosphere temperature increases with altitude. The temperature reversal is called the tropopause. The troposphere also differs from the stratosphere in having small-scale turbulence and a homogenous distribution of trace gases. The stratosphere has large, slow air movements and nonuniform trace gases. The region of high ozone concentration is called the ozonosphere.

ides. A molecule first enters into the atmospheric chemistry when it is attacked by a free radical and "broken open". The principal attacking radicals, hydroxyl (OH) radicals, are initially produced from ozone, sunlight, and water vapor. The rate at which the compound reacts with OH radicals is a major determiner of reactivity. The olefins react the fastest; propylene, for example, reacts about ten times faster than propane.

Ozone, which comes into the troposphere from the stratosphere, is photodissociated by ultraviolet sunlight, yielding an energetic oxygen atom (O*).



The excited oxygen atom then attacks water to yield two hydroxyl radicals.

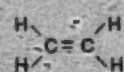


These OH radicals attack the hydrocarbons, starting an oxidation chain that involves intermediate peroxy radicals and carbonyl compounds such as aldehydes and ketones. The

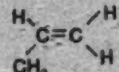
Paraffins, also called alkanes, are hydrocarbons consisting of continuous or branched chains of carbon atoms with hydrogen atoms satisfying carbon's valence requirements

Ethane:	C_2H_6	CH_3-CH_3
Propane:	C_3H_8	$CH_3-CH_2-CH_3$
Butane:	C_4H_{10}	$CH_3-CH_2-CH_2-CH_3$
Pentane:	C_5H_{12}	$CH_3-CH_2-CH_2-CH_2-CH_3$
Hexane:	C_6H_{14}	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

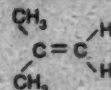
Olefins, or alkenes, are hydrocarbons with one or more carbon-carbon double bonds. The names of many olefinic compounds are derived from their simpler paraffinic counterparts



Ethylene: C_2H_4



Propylene: C_3H_6

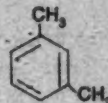


Isobutylene: C_4H_8

Aromatic compounds are benzene derivatives with high carbon-to-hydrogen ratios and a very stable core of six carbon atoms

Toluene: $C_6H_5CH_3$

Meta-xylene: $C_6H_4(CH_3)_2$



Carbonyl compounds, which include aldehydes and ketones, are characterized by a carbon-oxygen double bond

Formaldehyde: H_2CO



oxidation continues until all carbons and hydrogens have been converted to CO , CO_2 , and H_2O . The CO will eventually be converted to CO_2 , but only after a delay of several months.

The OH radicals break paraffinic (fully hydrogenated) molecules by hydrogen abstraction. The rate of the reaction depends on the strength of the $C-H$ bonds. The more hydrogens attached to a carbon, the stronger the $C-H$ bond, and the slower the hydrogen removal. On the average, a methane molecule released into the air will last about ten years. In contrast, ethane with six hydrogens, three on each of its primary carbons, will last about three months. Propane, with six primary hydrogens and two secondary hydrogens, will last two weeks. Isopentane, having 9 primary hydrogens, 2 secondary hydrogens, and one tertiary hydrogen, will last only five days. Hydrogens on the same carbon as a carbonyl oxygen, as in formaldehyde, are removed even faster than tertiary hydrogens of paraffins.

Olefins such as propylene are broken by addition of hydroxyl radicals to the double bond. OH addition and the subsequent oxidation proceed very rapidly. Propylene is the most reactive major constituent of auto exhaust, but

some other olefins react even faster than propylene. In the case of aromatics such as xylene, the OH may attack either by hydrogen abstraction or by addition. Details are yet to be worked out.

Nitrogen-Containing Compounds

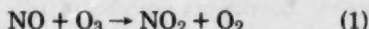
The photochemistry of the polluted troposphere develops around the nitrogen oxides, the key action being the photodissociation of NO_2 to yield NO molecules and O atoms. Reactions that follow then engage the organic material, leading to its oxidation and the formation of noxious by-products. NO and NO_2 are finally removed from the air in particles and droplets, largely as nitrate solutions.

Many millions of tons of NO and NO_2 of natural origin are present in the global atmosphere at any moment. In urban areas, however, the background amounts are trivial compared to man-made amounts. The general geophysical background concentration of NO_x (NO plus NO_2) is not greater than three or four parts per billion. About two-thirds of the NO found in large cities comes from cars and trucks while one third comes from stationary sources, mainly power plants. The proportions of NO and NO_2

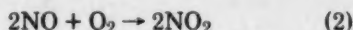
shift during the day as a result of photochemical action.

Lightning produces nitrogen oxides, but this appears to be a small source, even on a world-wide basis. The NO formed in the upper atmosphere can be neglected in considering human exposure, because so little of it propagates down into the lower troposphere. Oxidized nitrogen in the stratosphere exists mainly as nitric acid, HNO_3 , but as this acid migrates to the troposphere it is removed in precipitation. The tropospheric background concentration of HNO_3 vapor is so low that it has not even been measured. The exposure of urban populations to nitrogen-containing pollutants is almost entirely the result of nitrogen oxides formed in combustion processes.

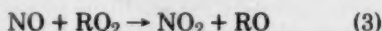
The chemical path from nitric oxide to nitrate begins with the oxidation of NO to NO_2 by three main oxidizers: ozone, oxygen, and peroxy radicals. The reaction of NO with ozone is extremely fast.



This is probably the major reaction of NO when it is emitted into ozone-containing atmospheres. The reaction of NO with molecular oxygen appears to be a trimolecular reaction and as such proceeds only very slowly when the NO is at low concentration.

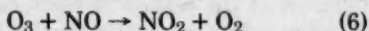
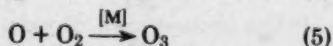
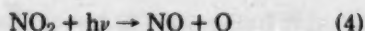


The reaction is too slow to be of importance in the ambient polluted air, but it may take place during the dilution of NO-containing effluents. It is partly responsible for the initial presence of NO_2 in the morning air of cities. Thirdly, NO reacts with peroxy radicals (RO_2)



Because of the low concentration of the radicals, only a small portion of the NO engages in this reaction. Nevertheless, the reaction plays an important role in the atmosphere.

NO_2 in the atmosphere absorbs sunlight and dissociates into NO and oxygen atoms. With the assistance of another molecule, M, the oxygen atoms combine with oxygen molecules, forming ozone. The ozone then reacts with NO, returning it to NO_2 .



Photodissociation will take place within one or two ~~months~~ ^{minutes} after the exposure of an NO_2 molecule to the sunlight. If there are no other impurities, however, the steady state concentration of NO_2 is changed very little by the cycle

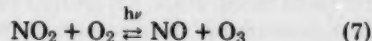


Courtesy Washington Post



On a clear day (above), Washington landmarks can be seen from the Virginia side of the Potomac. But on a smoggy day (below), visitors can catch only a glimpse of the Washington Monument's outlines, while the Capitol is completely obscured

because the reverse reactions (5) and (6) are so fast. In that case, photolysis may go on for a long time with no net change in composition.

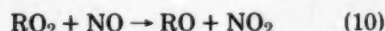
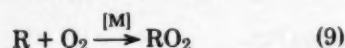
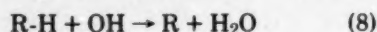


When other compounds are present, the composition is changed, although not in the direction one might normally expect. In the presence of impurities, photodissociation causes an increase in the concentration of NO_2 , rather than a decrease. This seemed paradoxical to the early investigators of urban photochemistry, but it soon became obvious that the

increase of NO_2 in the sunlit atmosphere resulted from the involvement of the organic pollutants in the photochemical process.

The Interaction of CH_x and NO_x

The formation of excess ozone, nitrogen dioxide, nitrates, and other noxious chemicals in the smog results from interactions between nitrogen oxides and organic materials. Hydrocarbons interact with the nitrogen-containing pollutants by way of free radicals. These radicals are produced in the attack on hydrocarbons by energetic species such as OH , O_2H , O_3 , and O . If the organic radicals are designated R , the general reaction scheme, using OH as the starter, can be written as follows:



This set of reactions disturbs the equilibrium reaction (7). The NO oxidation in reaction (10) takes the place of reaction (6), thus leaving a free ozone molecule. This ozone can then oxidize a second NO molecule if there is one available. If not, the ozone will remain in the atmosphere. In the early part of the day the hydrocarbons are therefore instrumental in converting NO to NO_2 , while later in the day, when NO_2 predominates, the hydrocarbons are responsible for generating excess ozone. The rate of photochemical action accelerates during the morning hours because radicals are regenerated and new species that are easily photooxidized are produced.

Noxious By-Products

The discovery of a family of peroxy acyl nitrates, PAN, was a remarkable aspect of the study of smog chemistry. Although these compounds have great importance in photochemical air pollution, they are unknown in any other aspect of chemistry. Peroxy acetyl nitrate is the principal member of the family and the only one regularly detected in the urban air. This compound received much publicity in the 1950s as the notorious "compound X" of photochemical smog. PAN, discovered in 1955 and first measured in the atmosphere in 1957, has been shown to be eye-irritating, plant-damaging, and poisonous to animals.

PAN is not photodissociated in the smog, but the compound does disappear from the polluted air during the night. Current research is showing that gaseous PAN dissociates thermally to yield peroxy acetate radicals and NO_2 at a rate fast enough for the dissociation to play a role in atmospheric chemistry. In the past two years

there has been a resurgence of interest in the chemistry of PAN-type compounds. Because PAN forms readily in the daytime but slowly releases its NO_2 at night, it may well be a "holding-tank" for NO_2 and an important source of conversion of NO released during the dark. The reactions of PAN are still much in need of study. Other peroxy nitrates are also of current interest, including peroxy nitric acid (HOONO_2) and alkyl peroxy nitrates.

In addition to ozone and PAN, other noxious by-products are produced in the photochemical reaction. Chief among these are fine particles containing partially oxidized organic matter, ammonium nitrate, and ammonium sulfate. If the pollution is especially heavy, the ammonia supply may fall short, leaving the sulfate in the ammonium bisulfate form or as sulfuric acid.

The fine particles that grow from the gases in the smog will lodge in the lungs, whereas many of the gases taken into the lungs will be exhaled. Furthermore, it is the particles, not the gases, that destroy visibility by light scattering. These particles are found to contain as major components both nitrates and sulfates, usually in ammoniated form. There is also a large organic component formed from oxidation of organic vapors to less volatile forms. In dusty areas there will be a silicon-containing component concentrated in the larger range of particle sizes.

Chemistry Summary

The chemistry of smog is summarized in the microcosm shown in Figure 2. Sunlight drives the NO_x -ozone engine shown at the center. Surrounding this central core of reactions are the satellite reactions involving the hydrocarbons. It is the interaction of the hydrocarbon system with the core NO_x system that causes the spin-out of such noxious products as ozone, peroxy compounds, nitrates, and sulfates. As the products are spun out, more fuel in the form of oxygen, hydrocarbons, and NO_x is drawn in. When the ignition by sunlight ceases, the engine stops. If fresh fuel accumulates during the night, the engine quickly gets up to speed again in the morning. If the fuel is blown away or thinned out by the wind, the engine runs very much slower.

What is Being Done or Should Be Done?

It was obvious even 20 years ago that curtailment of the release of hydrocarbons and nitrogen oxides from automobiles would substantially reduce urban smog. What was not so obvious was the best approach to this curtailment. Oxidation of the hydrocarbons in the exhaust system of a car appeared early in the study to be the most promising control strategy,

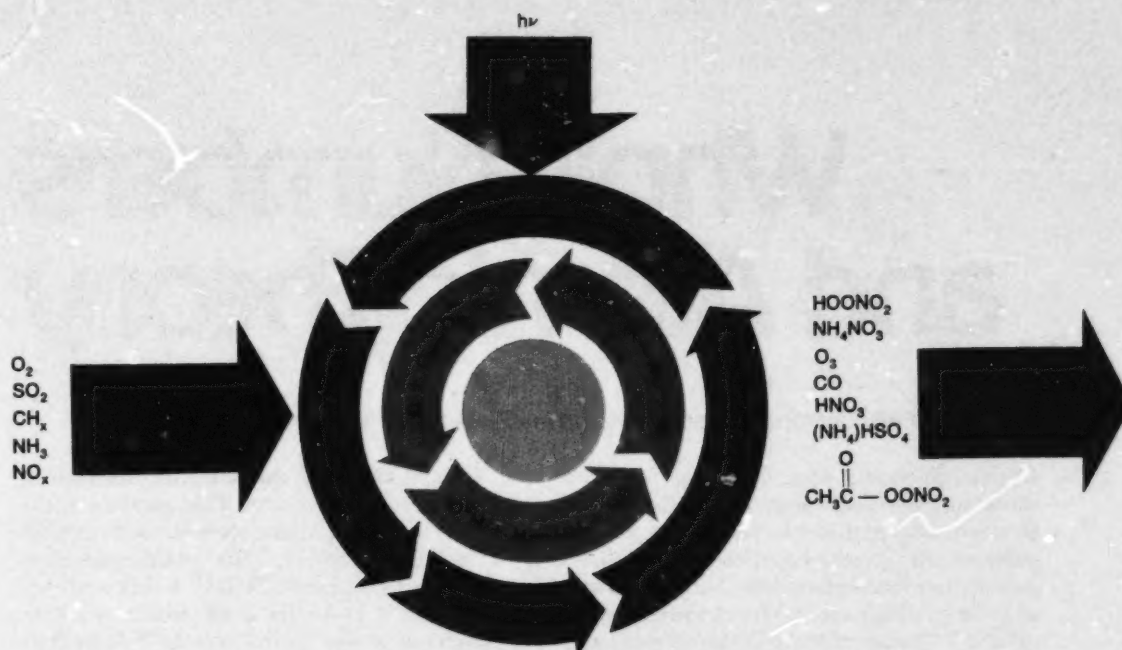


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sulfates. As these products are spun out, more fuel in the form of oxygen, hydrocarbons, and NO_x is drawn in. When ignition by sunlight ceases, the engine stops, but if fresh fuel accumulates during the night, the engine quickly gets up to speed again in the morning and the cycle begins again.

and that strategy has not yet been replaced by a better one. The catalytic muffler has been available since the time of the early investigations by Haagen-Smit and his contemporaries. There were some competing ideas, such as the flame afterburner, but none of these competitors seem to have survived the engineering tests of time. The catalytic muffler is now being used, along with certain engine changes that also reduce emissions. In addition, controls are being placed on the loss of gasoline in handling and on the release of organic vapors used as solvents and cleaners. The most reactive compounds are subject to the strictest control.

Restrictions are also being placed on the release of nitrogen oxides by automotive and industrial sources. These control actions have been developed and ordained under the Congressional Clean Air Act of 1967 with its amendments of 1970 and 1977. The imposition of controls has been a step-wise procedure over the past five or six years, with each succeeding year seeing stricter requirements. Already there are indications that the smog has lessened in some cities, but in many places photochemical

smog problems and other types of air pollution problems are still increasing. Although progress has been made, the study of atmospheric chemistry must continue. It is certain that there are many facts of that chemistry still to be discovered.

Suggested Reading

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- (3) Leighton, P., "Photochemistry of Air Pollution", Academic Press, NY, 1961.
- (4) Seinfeld, J. H., "Air Pollution, Physical and Chemical Fundamentals", McGraw-Hill, NY, 1975.

PHILIP HANST, during the past 25 years, has made fundamental contributions to our understanding of atmospheric photochemistry, the measurement of atmospheric trace gases, and the development of optical techniques of pollution measurement. He is currently directing a research program on the fate of halogenated pollutants in the troposphere and stratosphere and their interactions with stratospheric ozone.

